

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-302779

(43)Date of publication of application : 13.11.1998

(51)Int.Cl.

H01M 4/04

C01G 53/00

H01M 4/02

H01M 4/58

H01M 10/40

(21)Application number : 09-109782

(71)Applicant : SONY CORP

(22)Date of filing : 25.04.1997

(72)Inventor : ISONAGA TAISUKE

YAMAMOTO YOSHIKATSU

### (54) PRODUCTION OF POSITIVE ELECTRODE ACTIVE MATERIAL

#### (57)Abstract:

PROBLEM TO BE SOLVED: To reduce the deterioration of a battery characteristic under a high temperature environment by treating with a gas a lithium composite oxide of a specific composition in an atmosphere of specific CO<sub>2</sub> concentration and a dew point lower than a specific temperature, in a nonaqueous electrolytic secondary battery using the lithium composite oxide as a positive electrode active material.

SOLUTION: The lithium composite oxide expressed by the formula,  $\text{Li}_x\text{Ni}_y\text{M}_{(1-y)}\text{O}_2$  (M is at least one of transition metals B, Al, Ga, and In;  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ ) is treated with a gas in an atmosphere of CO<sub>2</sub> concentration  $\geq 0.1$  vol.% and a dew point  $\leq -15^\circ\text{C}$ . The lithium composite oxide may be gas treated in a gas atmosphere of CO<sub>2</sub> concentration  $\geq 0.1$  vol.% and a dew point  $\leq -15^\circ\text{C}$ , after the completion of baking or in a cooling stage after baking. In this treatment, the ambient temperature is preferably  $\leq 150^\circ\text{C}$ .

### LEGAL STATUS

[Date of request for examination] 17.09.2003

[Date of sending the examiner's decision of 27.09.2005 rejection]

[Kind of final disposal of application other

than the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number] 3769871

[Date of registration] 17.02.2006

[Number of appeal against examiner's  
decision of rejection] 2005-020813

[Date of requesting appeal against  
examiner's decision of rejection] 27.10.2005

[Date of extinction of right]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**CLAIMS**

---

[Claim(s)]

[Claim 1] General formula  $\text{Li}_x\text{Ni}_y\text{M}$  ( $1-y$ ) The manufacture approach of the positive active material characterized by carrying out gassing of the lithium multiple oxide expressed with  $\text{O}_2$  (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % and, whose dew-point is -15 degrees C or less.

[Claim 2] The manufacture approach of the positive active material according to claim 1 characterized by carrying out gassing of the above-mentioned lithium multiple oxide in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % after the completion of baking and, whose dew-point is -15 degrees C or less.

[Claim 3] The manufacture approach of the positive active material according to claim 1 characterized by carrying out gassing in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % in a cooling phase after calcinating the above-mentioned lithium multiple oxide and, whose dew-point is -15 degrees C or less.

[Claim 4] The manufacture approach of the positive active material according to claim 1 characterized by making the above-mentioned ambient temperature into 150 degrees C or less.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the positive active material used for the positive electrode of a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] High-performance-izing of electronic equipment, a miniaturization, and portable-ization progress by advance of an electronic technique in recent years, and the demand of the high energy consistency cell used for these electronic equipment has become strong. LiCoO<sub>2</sub> is used as a positive-electrode ingredient under such a situation, the rechargeable lithium-ion battery which used for the negative-electrode ingredient the carbon material in which a dope and a dedope of a lithium are possible is commercialized, and it is adopted as various portable electronic devices, such as a camcorder, a cellular phone, and a notebook sized personal computer.

[0003] Recently, this rechargeable lithium-ion battery is adopted as the electronic equipment used not only the bottom of an ordinary temperature environment but under the various environments from low temperature to an elevated temperature more often. In the notebook sized personal computer whose adoption is increasing especially recently, since the interior temperature of a personal computer becomes high with improvement in the speed of a central processing unit and long duration use of the built-in rechargeable lithium-ion battery is carried out under hot environments, the cell property under hot environments is important.

[0004] On the other hand, it is searched for the technique using LixNiyM(1-y) O<sub>2</sub> (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) which made nickel the subject as positive active material instead of LiCoO<sub>2</sub> for adequate supply of the raw material of this rechargeable lithium-ion battery.

[0005]

[Problem(s) to be Solved by the Invention] However, as for LixNiyM(1-y) O<sub>2</sub>, a lithium hydroxide and lithium oxide remain after composition. Therefore, since it had a bad influence on a cell property when these residues use it for the bottom of hot environments even if it uses this lithium nickel oxide as positive active material, sufficient preservation property was not able to be acquired under hot environments.

[0006] So, in JP,6-342657,A, it removes by rinsing the lithium hydroxide in the lithium multiple oxide after composition with the minimum water, and drying, and the method of avoiding a bad influence is indicated. However, the processing of rinsing is complicated and it is difficult to industrialize from re-desiccation being required. Furthermore, in JP,8-138649,A, it is supposed that it will be unstable for the moisture in an ambient atmosphere, and a lithium multiple oxide will be decomposed into it. For this reason, it is expected in the rechargeable lithium-ion battery

using the positive active material produced based on the example of JP,6-342657,A that degradation of a cell property is large.

[0007] This invention is proposed in order to solve the above troubles, it loses the effect of the lithium hydroxide and lithium oxide which remain in positive active material, and aims at offering the manufacture approach of the positive active material which becomes possible [ obtaining the nonaqueous electrolyte rechargeable battery which is high capacity and was excellent in the preservation property under hot environments ].

[0008]

[Means for Solving the Problem] In order that the manufacture approach of the positive active material concerning this invention may solve the above-mentioned purpose General formula  $\text{Li}_x\text{Ni}_y\text{M}_{1-x-y}\text{O}_2$  (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) It is characterized by carrying out gassing of the lithium multiple oxide expressed in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % and whose dew-point is -15 degrees C or less.

[0009] What is necessary is just to carry out a gas place to the above-mentioned lithium multiple oxide in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % after the completion of baking, or in the cooling phase after baking and whose dew-point is -15 degrees C or less. In addition, it faces performing this processing and it is desirable that ambient temperature is 150 degrees C or less.

[0010] Since the lithium hydroxide and lithium oxide which remain in a lithium multiple oxide are lithium-carbonate-ized according to the manufacture approach of the positive active material concerning this invention, this lithium multiple oxide can be set to the nonaqueous electrolyte rechargeable battery used as positive active material, and degradation of the cell property under hot environments can be made small. Moreover, since there is also no disassembly of the lithium multiple oxide by moisture like before since processes, such as rinsing, are not included, and a complicated process is not needed, industrialization is easy, and industrial value is large.

[0011] In addition, since the concentration of  $\text{CO}_2$  of an ambient atmosphere remains under by 0.1 volume %, without lithium-carbonate-izing lithium oxide and the lithium hydroxide in a lithium multiple oxide, it is not desirable. Moreover, if the dew-point of an ambient atmosphere exceeds -15 degrees C, since the decomposition reaction of a lithium multiple oxide will be promoted by moisture and it leads to the fall of capacity with it, it is not desirable. Furthermore, since the lithium multiple oxide itself decomposes and it leads to the fall of capacity when the temperature of an ambient atmosphere exceeds 150 degrees C, it is not desirable.

[0012]

[Embodiment of the Invention] Hereafter, the manufacture approach of the positive active material concerning this invention is explained to a detail.

[0013] First, mix lithium salt, nickel salt, and M salt (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In.), and this mixture is calcinated. General formula  $\text{Li}_x\text{Ni}_y\text{M}_{1-x-y}\text{O}_2$  (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) The lithium multiple oxide expressed is obtained. And gassing is performed in the ambient atmosphere whose  $\text{CO}_2$  concentration it is in the condition which returned to the room temperature after the completion of baking, or is more than 0.1 volume % to the above-mentioned lithium multiple oxide in the cooling phase after baking and whose dew-point is -15 degrees C or less.

[0014] Thereby, lithium oxide and the lithium hydroxide which remained in [ after compounding a lithium multiple oxide ] this lithium multiple oxide are lithium-carbonate-ized.

[0015] Consequently, since it comes to remove lithium oxide and the lithium hydroxide which were presupposed that it has a bad influence on the bottom of hot environments, the nonaqueous electrolyte rechargeable battery using the lithium multiple oxide after this processing as positive

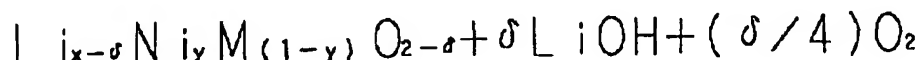
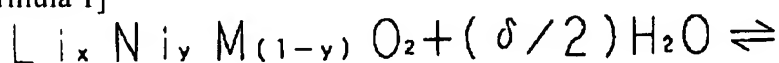
active material is excellent in a preservation property under hot environments, and becomes the thing of high capacity.

[0016] Here, if the concentration of CO<sub>2</sub> in an ambient atmosphere becomes under 0.1 volume %, the lithium hydroxide and lithium oxide which are not lithium-carbonate-ized in a lithium multiple oxide will remain. Consequently, the cell [ cell / which used this lithium manganic acid ghost as positive active material / nonaqueous electrolyte ] property under hot environments will fall. Therefore, it is necessary to carry out concentration of CO<sub>2</sub> of an ambient atmosphere to more than 0.1 volume %.

[0017] Moreover, if the dew-point in an ambient atmosphere exceeds -15 degrees C, the decomposition reaction of a lithium multiple oxide will be promoted by moisture, and it will lead to the fall of capacity with it. This will be considered that the decomposition reaction of a lithium multiple oxide will be promoted on the contrary if a lithium hydroxide is lithium-carbonate-ized in the condition that the decomposition reaction of a lithium multiple oxide is considered to be based on chemical equilibrium as shown in \*\* 1, and a lot of steams are in an ambient atmosphere. That is, the decomposition reaction of a lithium multiple oxide can be suppressed by performing gassing by CO<sub>2</sub> to the minimum, keeping the dew-point of an ambient atmosphere low and driving out moisture out of the system of reaction. Therefore, it is necessary to make the dew-point of the above-mentioned ambient atmosphere into -15 degrees C or less.

[0018]

[Formula 1]



[0019] Furthermore, as for the temperature of the above-mentioned ambient atmosphere, it is more desirable that it is 150 degrees C or less. Since the lithium multiple oxide itself decomposes and it leads to the fall of capacity when the temperature of an ambient atmosphere exceeds 150 degrees C, it is not desirable. Therefore, as mentioned above, gassing by CO<sub>2</sub> may be continuously performed, after ambient temperature becomes 150 degrees C or less in a cooling phase, although you may carry out in the condition of having returned to the room temperature after baking of a lithium multiple oxide.

[0020] by the way, the lithium multiple oxide obtained by the above manufacture approaches -- general -- after composition -- grinding -- the shape of powder -- carrying out -- binders, such as an electric conduction agent and rubber, a dispersant, etc. -- adding -- slurring -- after that and this mixture -- a slurry is applied to a charge collector or it is produced by a certain thing [ carrying out \*\* molding and making it a pellet type ].

[0021] Especially as the above-mentioned electric conduction agent, although it does not limit, metal powder, carbon powder, etc. are used. Especially, in carbon powder, pyrolytic carbon and its graphitization article, artificial and natural scale-like graphite powder, a carbon fiber, its graphitization articles, such as carbon black, etc. are used suitably. Moreover, the mixed elegance of these carbon powder is also used.

[0022] Moreover, although the lithium multiple oxide mentioned above is not limited to especially the negative-electrode ingredient combined with the positive electrode used as positive active material, polymers, such as a carbon material in which a dope and a dedope of a lithium, and a lithium alloy with aluminum, lead, an indium, etc. and a lithium are possible or polyacethylene, and polypyrrole, are used just possible [ a dope and a dedope of a lithium metal or a lithium ].

[0023] Especially as the above-mentioned carbon material used for a negative electrode, although it does not limit, pyrolytic carbon, corks, graphites (pitch coke, needle coke, petroleum coke, etc.), glassy carbon, an organic high-molecular-compound baking object (what calcinated phenol resin, furan resin, etc. at suitable temperature), a carbon fiber, activated carbon, etc. are usable.

[0024] Especially difficulty graphitized carbon is suitably used from the reasons of excelling in the cycle property that the charge-and-discharge capacity per weight is large. Also in this, the carbonaceous ingredient which the spacing of a field (002) is 0.370nm or more, and true density is less than three 1.70 g/cm, and does not have an exothermic peak at 700 degrees C or more by the differential thermal analysis in an air current is used.

[0025] The carbonaceous ingredient which carbonizes an organic material by technique, such as baking, and is obtained as an ingredient which has such a property is mentioned, and the furan resin which consists of furfuryl alcohol or a homopolymer of a furfural, and a copolymer is suitable as a start raw material of carbonization. Specifically, the polymer which becomes by furfural + phenol, furfuryl alcohol + dimethylolurea, furfuryl alcohol, and furfuryl alcohol + formaldehyde, furfuryl alcohol + furfural, and furfural + ketones is used preferably.

[0026] Or after introducing the functional group which contains oxygen in this, using the petroleum pitch of hydrogen / carbon atomic ratios 0.6-0.8 as a raw material, giving the so-called oxygen bridge formation and considering as the precursor of 10 - 20 % of the weight of oxygen contents, the carbonaceous ingredient calcinated and obtained is also suitable.

[0027] Furthermore, in case the above-mentioned furan resin, a petroleum pitch, etc. are carbonized, the carbonaceous ingredient which made the amount of dopes to a lithium big is also usable by adding phosphorus compounds or a boron compound.

[0028] the higher negative electrode as a graphite ingredient -- a mixture -- in order to obtain restoration nature, it is required for true specific gravity to be three or more 2.10 g/cm, and what is three or more 2.18 g/cm is used suitably. In order to obtain such true specific gravity, it is required for the spacings acquired with an X-ray diffraction method to be 0.335nm or more and 0.34nm or less, and it is more desirable that they are 0.335nm or more and 0.337nm or less. As for the crystal thickness of the direction of a c-axis, it is desirable that it is 16.0nm or more, and it is more desirable that it is 24.0nm or more.

[0029] Furthermore, each well-known thing can be conventionally used for other components used combining the positive electrode and negative electrode which were mentioned above, for example, nonaqueous electrolyte, and a separator.

[0030] As nonaqueous electrolyte, lithium salt is used as an electrolyte and the electrolytic solution made to dissolve this in an organic solvent is used, for example. Here, especially as an organic solvent, although it does not limit, independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, gamma-butyrolactone, diethylether, a tetrahydrofuran, a 2-methyl-tetrahydrofuran, 1, 3-dioxolane, a sulfolane, an acetonitrile, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methylethyl carbonate, and methylpropyl carbonate, are used.

[0031] As a separator, textile fabrics, a nonwoven fabric, the synthetic-resin fine porosity film, etc. are mentioned. Although the synthetic-resin fine porosity film is used especially suitably, the polyolefine system fine porosity film is suitably used in respect of thickness, film reinforcement,

membrane resistance, etc. also in it. Specifically, polyethylene and the fine porosity film made from polypropylene, or the fine porosity film that compounded these is used.

[0032] As a charge collector of a positive electrode, for example, aluminum, stainless steel, nickel, etc. can be used, and reticulated things, such as the shape of a foil, a mesh, and an expanded metal, are desirable as the configuration. As thickness, a 10-50-micrometer thing is used suitably. As the quality of the material used for a negative-electrode charge collector, it is desirable to, use copper, stainless steel, nickel, etc. for example. As thickness, a 5-30-micrometer thing is used suitably.

[0033] Moreover, in order to obtain a closed mold nonaqueous electrolyte rechargeable battery with more high safety, it is desirable to have means, such as a relief valve which it operates [ relief valve ] by cell internal pressure rise, and makes a current intercept at the time of abnormalities, such as overcharge.

[0034]

[Example] the range which this invention is not limited at all by this example, and does not change the main point although the concrete example which applied this invention is hereafter explained based on an experimental result -- it is possible to be, to change suitably and to carry out.

[0035] an example 1 -- first, as shown in introduction and drawing 1 , the positive electrode 1 was produced as follows. A lithium hydroxide, nickel oxide, and cobalt oxide were mixed with the ball mill so that it might be set to Li/nickel/Co=1.01/0.80/0.20 by the mole ratio, and it calcinated for 750 more degree C and 10 hours, after carrying out temporary quenching in 100% oxygen for 450 degree C and 5 hours. And CO<sub>2</sub> concentration carried out gassing at the room temperature (23 degrees C) for 5 hours among the ambient atmosphere whose dew-point are after baking termination and is 0.1 volume % at -15 degrees C, and positive active material was obtained.

[0036] next, this positive active material by which gassing was carried out -- grinding -- this positive active material -- as 91 % of the weight and an electric conduction agent -- graphite -- as 6 % of the weight and a binder -- polyvinylidene fluoride -- 3 % of the weight -- mixing -- a positive electrode -- a mixture is prepared and it distributes to a N-methyl-2-pyrrolidone -- making -- a positive electrode -- a mixture -- it considered as the slurry. and this positive electrode -- a mixture -- the slurry was applied to the aluminium foil used as the positive-electrode charge collector 10, and the positive electrode 1 band-like by carrying out compression molding with a roller-press machine was produced after desiccation.

[0037] Next, the negative electrode 2 was produced as follows. The petroleum pitch was used for the start raw material, after carrying out installation (oxygen bridge formation) of the functional group which contains oxygen in this 10 to 20%, it calcinated at the temperature of 1000 degrees C among inert gas, and the negative-electrode active material was obtained. This obtained negative-electrode active material is a difficulty graphitized-carbon ingredient near a vitrified carbon material. this carbonaceous ingredient -- as 90 % of the weight and a binder -- 10 % of the weight of polyvinylidene fluorides -- mixing -- a negative electrode -- a mixture is prepared and it distributes to a N-methyl-2-pyrrolidone -- making -- a negative electrode -- a mixture -- it considered as the slurry. and this negative electrode -- a mixture -- the negative electrode 2 band-like by carrying out compression molding of the slurry with a roll press machine after spreading and desiccation to both sides of the copper foil used as the negative-electrode charge collector 11 was obtained.

[0038] The swirl type electrode object was produced by carrying out the laminating of the positive electrode 1 and negative electrode 2 which were produced as mentioned above to order, and winding them around it many times through the separator 3 which consists of a fine porosity polypropylene film with a thickness of 25 micrometers. In addition, with this swirl type electrode



object, the negative electrode 2 considered as a dimension to which width of face and die length serve as size from a positive electrode 1.

[0039] Thus, the produced swirl type electrode object was contained with the iron cell can 5 which performed nickel plating, and the electric insulating plate 4 has been arranged to vertical both sides of a swirl type electrode object. And in order to perform current collection of a positive electrode 1 and a negative electrode 2, the aluminum lead 12 was drawn from the positive-electrode charge collector 10, and it welded to the relief valve equipment 8 connected with the cell lid 7 through the PTC component 9, and the nickel lead 13 was drawn from the negative-electrode charge collector 11, and it welded to the cell can 5. And the electrolytic solution made to dissolve LiPF<sub>6</sub> [ one-mol ] in the mixed solvent of propylene carbonate 50 capacity % and diethyl carbonate 50 capacity % was poured in into the cell can 5. Subsequently, the cell lid 7 was fixed by closing the cell lid 7 and the cell can 5 through the obturation gasket 6 which applied asphalt, and the cylindrical cell with a diameter [ of 18mm ] and a height of 65mm shown in drawing 1 was produced.

[0040] Positive active material was calcinated like example 2 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 5 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0041] Positive active material was calcinated like example 3 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 10 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0042] Positive active material was calcinated like example 4 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 50 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0043] Positive active material was calcinated like example 5 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 100 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0044] Positive active material was calcinated like example 6 example 1, gassing was performed in the ambient atmosphere which changed 150 degrees C and CO<sub>2</sub> concentration into 10 volume % for processing temperature, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0045] Example 7 lithium hydroxide, nickel oxide, cobalt oxide, and a lithium hydroxide were mixed with the ball mill so that it might be set to Li/nickel/Co/aluminum(mole ratio) = 1.01/0.80/0.15/0.05, positive active material was calcinated like the example 1 after that, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 10 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0046] Positive active material was produced like example of comparison 1 example 1, and the dew-point performed gassing by having made into the ambient atmosphere air (CO<sub>2</sub> concentration being 0.03 volume %.) which is -15 degrees C or less, and produced the cylindrical cell by the same approach as an example 1 hereafter.

[0047] Positive active material was calcinated like example of comparison 2 example 1, gassing was performed in the ambient atmosphere which changed 0 degree C and CO<sub>2</sub> concentration into 10 volume % for the dew-point, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0048] Positive active material was calcinated like example of comparison 3 example 1, gassing was performed in the ambient atmosphere which changed 6 degrees C and CO<sub>2</sub> concentration into 10 volume % for the dew-point, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0049] Positive active material was calcinated like example of experiment 1 example 1, gassing

was performed in the ambient atmosphere which changed 200 degrees C and CO<sub>2</sub> concentration into 10 volume % for processing temperature, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0050] As mentioned above, about the positive active material compounded in the example, the example of a comparison, and the example of an experiment which were mentioned above, when X diffraction measurement was performed, the diffraction peak of a lithium carbonate was able to be checked except for the example 1 of a comparison. Moreover, the amount of lithium carbonates which remains in such positive active material was measured. After the amount of lithium carbonates in positive active material disassembled positive active material with the sulfuric acid, introduced generated CO<sub>2</sub> into barium chloride and a sodium-hydroxide solution and made it absorb, by titrating with a hydrochloric-acid standard solution, it carried out the quantum of the CO<sub>2</sub> amount, and converted and calculated it from the CO<sub>2</sub> amount.

[0051] Next, the capacity maintenance factor after preservation was measured under hot environments about the produced cylindrical cell. The capacity maintenance factor after preservation is a ratio when saving a cylindrical cell for 50 days under an environment with a temperature of 45 degrees C, measuring the discharge capacity at the time of 5 cycle  
\*\*\*\*\*, and \*\* (ing) discharge capacity of 5 cycle eye by initial capacity under hot environments.

[0052] The result of the capacity maintenance factor under the amount of these residual lithium carbonates and hot environments is shown in Table 1.

[0053]

[Table 1]

	CO <sub>2</sub> 濃度 (体積%)	露点 (°C)	処理温度 (°C)	残存炭酸リチウム量 (重量%)	容量維持率 (%)
実施例 1	0.1	-15	23	0.42	92
実施例 2	5	-15	23	0.43	93
実施例 3	10	-15	23	0.42	95
実施例 4	50	-15	23	0.42	94
実施例 5	100	-15	23	0.44	92
実施例 6	10	-15	150	0.42	92
実施例 7	10	-15	23	0.42	91
比較例 1	0.03	-15	23	0.06	75
比較例 2	10	0	23	0.66	76
比較例 3	10	6	23	0.72	74
実験例 1	10	-15	200	0.76	74

[0054] From an X diffraction measurement result and the result of Table 1, it is thought by carrying out concentration of CO<sub>2</sub> in an ambient atmosphere to more than 0.1 volume % that the lithium hydroxide and lithium oxide which remain in positive active material were able to be lithium-carbonate-ized.

[0055] The amount of residual lithium carbonates has little CO<sub>2</sub> concentration of an ambient atmosphere at 0.03 volume %, and the capacity maintenance factor under hot environments is also smaller than the time of CO<sub>2</sub> concentration being 0.1 volume % so that the result of the example 1 of a comparison may show on the other hand. There are many the lithium hydroxides and lithium oxide with which CO<sub>2</sub> concentration remains in 0.03 volume %, without being

lithium-carbonate-ized in positive active material, consequently it thinks that the capacity maintenance factor under hot environments also falls, and this is \*\*\*\*.

[0056] Moreover, if the result of the example 2 of a comparison and the example 3 of a comparison is seen, there are many amounts of residual lithium carbonates, and the capacity maintenance factor is small. Since the dew-point is high, this is guessed because positive active material decomposed, a decomposition product and CO<sub>2</sub> reacted and the amount of lithium carbonates has increased with the moisture in an ambient atmosphere. Furthermore, since the positive active material itself has decomposed, it is surmised that the capacity maintenance factor became small.

[0057] Furthermore, in the example 1 of an experiment, although temperature of an ambient atmosphere was made into 200 degrees C, there are many amounts of residual lithium carbonates, and the capacity maintenance factor is small. In a temperature field higher than 150 degrees C, the decomposition reaction of positive active material occurs and this is conjectured that a decomposition product and CO<sub>2</sub> reacted and the amount of lithium carbonates has increased. Since the positive active material itself has furthermore decomposed, it is surmised that the capacity maintenance factor became small. Therefore, as for the temperature of an ambient atmosphere, it is desirable that it is 150 degrees C or less.

[0058] The lithium hydroxide and lithium oxide in positive active material can be lithium-carbonate-ized by carrying out CO<sub>2</sub> concentration in [ after calcinating a lithium multiple oxide ] an ambient atmosphere to more than 0.1 volume %, and making a dew-point into -15 degrees C or less from these results, and it turns out that the nonaqueous electrolyte rechargeable battery using this positive active material can obtain a high capacity maintenance factor under hot environments. Furthermore, gassing by CO<sub>2</sub> is understood that it is desirable to carry out below 150 degrees C.

[0059]

[Effect of the Invention] Since it comes to carry out carbonic acid lithiation of the lithium hydroxide and lithium oxide which remain in positive active material according to the manufacture approach of the positive active material concerning this invention so that clearly also from the above explanation, the nonaqueous electrolyte rechargeable battery using this positive active material is excellent in an elevated-temperature preservation property, and will become high capacity. Moreover, since the manufacture approach of the positive active material concerning this invention does not have disassembly of the positive active material in processes, such as rinsing,, either and does not need a complicated process, its industrial value is large.

---

[Translation done.]

**\* NOTICES \***

**JPO and INPIT are not responsible for any damages caused by the use of this translation.**

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**TECHNICAL FIELD**

---

[Field of the Invention] This invention relates to the manufacture approach of the positive active material used for the positive electrode of a nonaqueous electrolyte rechargeable battery.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

PRIOR ART

---

[Description of the Prior Art] High-performance-izing of electronic equipment, a miniaturization, and portable-ization progress by advance of an electronic technique in recent years, and the demand of the high energy consistency cell used for these electronic equipment has become strong. LiCoO<sub>2</sub> is used as a positive-electrode ingredient under such a situation, the rechargeable lithium-ion battery which used for the negative-electrode ingredient the carbon material in which a dope and a dedope of a lithium are possible is commercialized, and it is adopted as various portable electronic devices, such as a camcorder, a cellular phone, and a notebook sized personal computer.

[0003] Recently, this rechargeable lithium-ion battery is adopted as the electronic equipment used not only the bottom of an ordinary temperature environment but under the various environments from low temperature to an elevated temperature more often. In the notebook sized personal computer whose adoption is increasing especially recently, since the interior temperature of a personal computer becomes high with improvement in the speed of a central processing unit and long duration use of the built-in rechargeable lithium-ion battery is carried out under hot environments, the cell property under hot environments is important.

[0004] On the other hand, it is searched for the technique using  $\text{Li}_x\text{Ni}_y\text{M}_{(1-y)}\text{O}_2$  (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) which made nickel the subject as positive active material instead of LiCoO<sub>2</sub> for adequate supply of the raw material of this rechargeable lithium-ion battery.

---

[Translation done.]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**EFFECT OF THE INVENTION**

---

[Effect of the Invention] Since it comes to carry out carbonic acid lithiation of the lithium hydroxide and lithium oxide which remain in positive active material according to the manufacture approach of the positive active material concerning this invention so that clearly also from the above explanation, the nonaqueous electrolyte rechargeable battery using this positive active material is excellent in an elevated-temperature preservation property, and will become high capacity. Moreover, since the manufacture approach of the positive active material concerning this invention does not have disassembly of the positive active material in processes, such as rinsing,, either and does not need a complicated process, its industrial value is large.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention] However, as for  $\text{Li}_x\text{Ni}_y\text{M}(1-y)\text{O}_2$ , a lithium hydroxide and lithium oxide remain after composition. Therefore, since it had a bad influence on a cell property when these residues use it for the bottom of hot environments even if it uses this lithium nickel oxide as positive active material, sufficient preservation property was not able to be acquired under hot environments.

[0006] So, in JP,6-342657,A, it removes by rinsing the lithium hydroxide in the lithium multiple oxide after composition with the minimum water, and drying, and the method of avoiding a bad influence is indicated. However, the processing of rinsing is complicated and it is difficult to industrialize from re-desiccation being required. Furthermore, in JP,8-138649,A, it is supposed that it will be unstable for the moisture in an ambient atmosphere, and a lithium multiple oxide will be decomposed into it. For this reason, it is expected in the rechargeable lithium-ion battery using the positive active material produced based on the example of JP,6-342657,A that degradation of a cell property is large.

[0007] This invention is proposed in order to solve the above troubles, it loses the effect of the lithium hydroxide and lithium oxide which remain in positive active material, and aims at offering the manufacture approach of the positive active material which becomes possible [ obtaining the nonaqueous electrolyte rechargeable battery which is high capacity and was excellent in the preservation property under hot environments ].

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

MEANS

---

[Means for Solving the Problem] In order that the manufacture approach of the positive active material concerning this invention may solve the above-mentioned purpose General formula  $\text{Li}_x\text{Ni}_y\text{M} (1-y) \text{O}_2$  (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) It is characterized by carrying out gassing of the lithium multiple oxide expressed in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % and whose dew-point is -15 degrees C or less.

[0009] What is necessary is just to carry out a gas place to the above-mentioned lithium multiple oxide in the ambient atmosphere whose  $\text{CO}_2$  concentration is more than 0.1 volume % after the completion of baking, or in the cooling phase after baking and whose dew-point is -15 degrees C or less. In addition, it faces performing this processing and it is desirable that ambient temperature is 150 degrees C or less.

[0010] Since the lithium hydroxide and lithium oxide which remain in a lithium multiple oxide are lithium-carbonate-ized according to the manufacture approach of the positive active material concerning this invention, this lithium multiple oxide can be set to the nonaqueous electrolyte rechargeable battery used as positive active material, and degradation of the cell property under hot environments can be made small. Moreover, since there is also no disassembly of the lithium multiple oxide by moisture like before since processes, such as rinsing, are not included, and a complicated process is not needed, industrialization is easy, and industrial value is large.

[0011] In addition, since the concentration of  $\text{CO}_2$  of an ambient atmosphere remains under by 0.1 volume %, without lithium-carbonate-izing lithium oxide and the lithium hydroxide in a lithium multiple oxide, it is not desirable. Moreover, if the dew-point of an ambient atmosphere exceeds -15 degrees C, since the decomposition reaction of a lithium multiple oxide will be promoted by moisture and it leads to the fall of capacity with it; it is not desirable. Furthermore, since the lithium multiple oxide itself decomposes and it leads to the fall of capacity when the temperature of an ambient atmosphere exceeds 150 degrees C, it is not desirable.

[0012]

[Embodiment of the Invention] Hereafter, the manufacture approach of the positive active material concerning this invention is explained to a detail.

[0013] First, mix lithium salt, nickel salt, and M salt (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In.), and this mixture is calcinated. General formula  $\text{Li}_x\text{Ni}_y\text{M} (1-y) \text{O}_2$  (however, M expresses at least one sort in transition metals, and B, aluminum, Ga and In, and is  $0.05 \leq x \leq 1.10$  and  $0.7 \leq y \leq 1.0$ .) The lithium multiple oxide expressed is obtained. And gassing is performed in the ambient atmosphere whose  $\text{CO}_2$  concentration it is in the condition which returned to the room temperature after the completion of baking, or is more than 0.1 volume % to the above-mentioned lithium multiple oxide in the cooling phase after baking and whose dew-point is -15 degrees C or less.

[0014] Thereby, lithium oxide and the lithium hydroxide which remained in [ after compounding



a lithium multiple oxide ] this lithium multiple oxide are lithium-carbonate-ized.

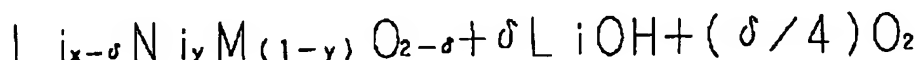
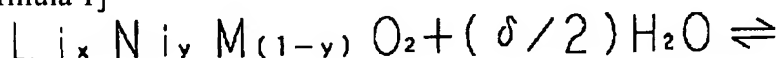
[0015] Consequently, since it comes to remove lithium oxide and the lithium hydroxide which were presupposed that it has a bad influence on the bottom of hot environments, the nonaqueous electrolyte rechargeable battery using the lithium multiple oxide after this processing as positive active material is excellent in a preservation property under hot environments, and becomes the thing of high capacity.

[0016] Here, if the concentration of CO<sub>2</sub> in an ambient atmosphere becomes under 0.1 volume %, the lithium hydroxide and lithium oxide which are not lithium-carbonate-ized in a lithium multiple oxide will remain. Consequently, the cell [ cell / which used this lithium manganic acid ghost as positive active material / nonaqueous electrolyte ] property under hot environments will fall. Therefore, it is necessary to carry out concentration of CO<sub>2</sub> of an ambient atmosphere to more than 0.1 volume %.

[0017] Moreover, if the dew-point in an ambient atmosphere exceeds -15 degrees C, the decomposition reaction of a lithium multiple oxide will be promoted by moisture, and it will lead to the fall of capacity with it. This will be considered that the decomposition reaction of a lithium multiple oxide will be promoted on the contrary if a lithium hydroxide is lithium-carbonate-ized in the condition that the decomposition reaction of a lithium multiple oxide is considered to be based on chemical equilibrium as shown in \*\* 1, and a lot of steams are in an ambient atmosphere. That is, the decomposition reaction of a lithium multiple oxide can be suppressed by performing gassing by CO<sub>2</sub> to the minimum, keeping the dew-point of an ambient atmosphere low and driving out moisture out of the system of reaction. Therefore, it is necessary to make the dew-point of the above-mentioned ambient atmosphere into -15 degrees C or less.

[0018]

[Formula 1]



[0019] Furthermore, as for the temperature of the above-mentioned ambient atmosphere, it is more desirable that it is 150 degrees C or less. Since the lithium multiple oxide itself decomposes and it leads to the fall of capacity when the temperature of an ambient atmosphere exceeds 150 degrees C, it is not desirable. Therefore, as mentioned above, gassing by CO<sub>2</sub> may be continuously performed, after ambient temperature becomes 150 degrees C or less in a cooling phase, although you may carry out in the condition of having returned to the room temperature after baking of a lithium multiple oxide.

[0020] by the way, the lithium multiple oxide obtained by the above manufacture approaches -- general -- after composition -- grinding -- the shape of powder -- carrying out -- binders, such as an electric conduction agent and rubber, a dispersant, etc. -- adding -- slurring -- after that and this mixture -- a slurry is applied to a charge collector or it is produced by a certain thing [ carrying out \*\* molding and making it a pellet type ].

[0021] Especially as the above-mentioned electric conduction agent, although it does not limit,

metal powder, carbon powder, etc. are used. Especially, in carbon powder, pyrolytic carbon and its graphitization article, artificial and natural scale-like graphite powder, a carbon fiber, its graphitization articles, such as carbon black, etc. are used suitably. Moreover, the mixed elegance of these carbon powder is also used.

[0022] Moreover, although the lithium multiple oxide mentioned above is not limited to especially the negative-electrode ingredient combined with the positive electrode used as positive active material, polymers, such as a carbon material in which a dope and a dedope of a lithium, and a lithium alloy with aluminum, lead, an indium, etc. and a lithium are possible or polyacethylene, and polypyrrole, are used just possible [ a dope and a dedope of a lithium metal or a lithium ].

[0023] Especially as the above-mentioned carbon material used for a negative electrode, although it does not limit, pyrolytic carbon, corks, graphites (pitch coke, needle coke, petroleum coke, etc.), glassy carbon, an organic high-molecular-compound baking object (what calcinated phenol resin, furan resin, etc. at suitable temperature), a carbon fiber, activated carbon, etc. are usable.

[0024] Especially difficulty graphitized carbon is suitably used from the reasons of excelling in the cycle property that the charge-and-discharge capacity per weight is large. Also in this, the carbonaceous ingredient which the spacing of a field (002) is 0.370nm or more, and true density is less than three 1.70 g/cm, and does not have an exothermic peak at 700 degrees C or more by the differential thermal analysis in an air air current is used.

[0025] The carbonaceous ingredient which carbonizes an organic material by technique, such as baking, and is obtained as an ingredient which has such a property is mentioned, and the furan resin which consists of furfuryl alcohol or a homopolymer of a furfural, and a copolymer is suitable as a start raw material of carbonization. Specifically, the polymer which becomes by furfural + phenol, furfuryl alcohol + dimethylolurea, furfuryl alcohol, and furfuryl alcohol + formaldehyde, furfuryl alcohol + furfural, and furfural + ketones is used preferably.

[0026] Or after introducing the functional group which contains oxygen in this, using the petroleum pitch of hydrogen / carbon atomic ratios 0.6-0.8 as a raw material, giving the so-called oxygen bridge formation and considering as the precursor of 10 - 20 % of the weight of oxygen contents, the carbonaceous ingredient calcinated and obtained is also suitable.

[0027] Furthermore, in case the above-mentioned furan resin, a petroleum pitch, etc. are carbonized, the carbonaceous ingredient which made the amount of dopes to a lithium big is also usable by adding phosphorus compounds or a boron compound.

[0028] the higher negative electrode as a graphite ingredient -- a mixture -- in order to obtain restoration nature, it is required for true specific gravity to be three or more 2.10 g/cm, and what is three or more 2.18 g/cm is used suitably. In order to obtain such true specific gravity, it is required for the spacings acquired with an X-ray diffraction method to be 0.335nm or more and 0.34nm or less, and it is more desirable that they are 0.335nm or more and 0.337nm or less. As for the crystal thickness of the direction of a c-axis, it is desirable that it is 16.0nm or more, and it is more desirable that it is 24.0nm or more.

[0029] Furthermore, each well-known thing can be conventionally used for other components used combining the positive electrode and negative electrode which were mentioned above, for example, nonaqueous electrolyte, and a separator.

[0030] As nonaqueous electrolyte, lithium salt is used as an electrolyte and the electrolytic solution made to dissolve this in an organic solvent is used, for example. Here, especially as an organic solvent, although it does not limit, independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, gamma-butyrolactone, diethylether, a tetrahydrofuran, a 2-methyl-tetrahydrofuran, 1, 3-dioxolane, a sulfolane, an acetonitrile, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, methylethyl carbonate,

and methylpropyl carbonate, are used.

[0031] As a separator, textile fabrics, a nonwoven fabric, the synthetic-resin fine porosity film, etc. are mentioned. Although the synthetic-resin fine porosity film is used especially suitably, the polyolefine system fine porosity film is suitably used in respect of thickness, film reinforcement, membrane resistance, etc. also in it. Specifically, polyethylene and the fine porosity film made from polypropylene, or the fine porosity film that compounded these is used.

[0032] As a charge collector of a positive electrode, for example, aluminum, stainless steel, nickel, etc. can be used, and reticulated things, such as the shape of a foil, a mesh, and an expanded metal, are desirable as the configuration. As thickness, a 10-50-micrometer thing is used suitably. As the quality of the material used for a negative-electrode charge collector, it is desirable to, use copper, stainless steel, nickel, etc. for example. As thickness, a 5-30-micrometer thing is used suitably.

[0033] Moreover, in order to obtain a closed mold nonaqueous electrolyte rechargeable battery with more high safety, it is desirable to have means, such as a relief valve which it operates [ relief valve ] by cell internal pressure rise, and makes a current intercept at the time of abnormalities, such as overcharge.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

EXAMPLE

---

[Example] the range which this invention is not limited at all by this example, and does not change the main point although the concrete example which applied this invention is hereafter explained based on an experimental result -- it is possible to be, to change suitably and to carry out.

[0035] an example 1 -- first, as shown in introduction and drawing 1 , the positive electrode 1 was produced as follows. A lithium hydroxide, nickel oxide, and cobalt oxide were mixed with the ball mill so that it might be set to Li/nickel/Co=1.01/0.80/0.20 by the mole ratio, and it calcinated for 750 more degree C and 10 hours, after carrying out temporary quenching in 100% oxygen for 450 degree C and 5 hours. And CO<sub>2</sub> concentration carried out gassing at the room temperature (23 degrees C) for 5 hours among the ambient atmosphere whose dew-point are after baking termination and is 0.1 volume % at -15 degrees C, and positive active material was obtained.

[0036] next, this positive active material by which gassing was carried out -- grinding -- this positive active material -- as 91 % of the weight and an electric conduction agent -- graphite -- as 6 % of the weight and a binder -- polyvinylidene fluoride -- 3 % of the weight -- mixing -- a positive electrode -- a mixture is prepared and it distributes to a N-methyl-2-pyrrolidone -- making -- a positive electrode -- a mixture -- it considered as the slurry. and this positive electrode -- a mixture -- the slurry was applied to the aluminium foil used as the positive-electrode charge collector 10, and the positive electrode 1 band-like by carrying out compression molding with a roller-press machine was produced after desiccation.

[0037] Next, the negative electrode 2 was produced as follows. The petroleum pitch was used for the start raw material, after carrying out installation (oxygen bridge formation) of the functional group which contains oxygen in this 10 to 20%, it calcinated at the temperature of 1000 degrees C among inert gas, and the negative-electrode active material was obtained. This obtained negative-electrode active material is a difficulty graphitized-carbon ingredient near a vitrified carbon material. this carbonaceous ingredient -- as 90 % of the weight and a binder -- 10 % of the weight of polyvinylidene fluorides -- mixing -- a negative electrode -- a mixture is prepared and it distributes to a N-methyl-2-pyrrolidone -- making -- a negative electrode -- a mixture -- it considered as the slurry. and this negative electrode -- a mixture -- the negative electrode 2 band-like by carrying out compression molding of the slurry with a roll press machine after spreading and desiccation to both sides of the copper foil used as the negative-electrode charge collector 11 was obtained.

[0038] The swirl type electrode object was produced by carrying out the laminating of the positive electrode 1 and negative electrode 2 which were produced as mentioned above to order, and winding them around it many times through the separator 3 which consists of a fine porosity polypropylene film with a thickness of 25 micrometers. In addition, with this swirl type electrode object, the negative electrode 2 considered as a dimension to which width of face and die length

serve as size from a positive electrode 1.

[0039] Thus, the produced swirl type electrode object was contained with the iron cell can 5 which performed nickel plating, and the electric insulating plate 4 has been arranged to vertical both sides of a swirl type electrode object. And in order to perform current collection of a positive electrode 1 and a negative electrode 2, the aluminum lead 12 was drawn from the positive-electrode charge collector 10, and it welded to the relief valve equipment 8 connected with the cell lid 7 through the PTC component 9, and the nickel lead 13 was drawn from the negative-electrode charge collector 11, and it welded to the cell can 5. And the electrolytic solution made to dissolve LiPF<sub>6</sub> [ one-mol ] in the mixed solvent of propylene carbonate 50 capacity % and diethyl carbonate 50 capacity % was poured in into the cell can 5. Subsequently, the cell lid 7 was fixed by closing the cell lid 7 and the cell can 5 through the obturation gasket 6 which applied asphalt, and the cylindrical cell with a diameter [ of 18mm ] and a height of 65mm shown in drawing 1 was produced.

[0040] Positive active material was calcinated like example 2 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 5 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0041] Positive active material was calcinated like example 3 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 10 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0042] Positive active material was calcinated like example 4 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 50 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0043] Positive active material was calcinated like example 5 example 1, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 100 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0044] Positive active material was calcinated like example 6 example 1, gassing was performed in the ambient atmosphere which changed 150 degrees C and CO<sub>2</sub> concentration into 10 volume % for processing temperature, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0045] Example 7 lithium hydroxide, nickel oxide, cobalt oxide, and a lithium hydroxide were mixed with the ball mill so that it might be set to Li/nickel/Co/aluminum(mole ratio) =1.01/0.80/0.15/0.05, positive active material was calcinated like the example 1 after that, gassing was performed in the ambient atmosphere which changed only CO<sub>2</sub> concentration into 10 volume %, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0046] Positive active material was produced like example of comparison 1 example 1, and the dew-point performed gassing by having made into the ambient atmosphere air (CO<sub>2</sub> concentration being 0.03 volume %.) which is -15 degrees C or less, and produced the cylindrical cell by the same approach as an example 1 hereafter.

[0047] Positive active material was calcinated like example of comparison 2 example 1, gassing was performed in the ambient atmosphere which changed 0 degree C and CO<sub>2</sub> concentration into 10 volume % for the dew-point, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0048] Positive active material was calcinated like example of comparison 3 example 1, gassing was performed in the ambient atmosphere which changed 6 degrees C and CO<sub>2</sub> concentration into 10 volume % for the dew-point, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0049] Positive active material was calcinated like example of experiment 1 example 1, gassing was performed in the ambient atmosphere which changed 200 degrees C and CO<sub>2</sub> concentration

into 10 volume % for processing temperature, and the cylindrical cell was hereafter produced by the same approach as an example 1.

[0050] As mentioned above, about the positive active material compounded in the example, the example of a comparison, and the example of an experiment which were mentioned above, when X diffraction measurement was performed, the diffraction peak of a lithium carbonate was able to be checked except for the example 1 of a comparison. Moreover, the amount of lithium carbonates which remains in such positive active material was measured. After the amount of lithium carbonates in positive active material disassembled positive active material with the sulfuric acid, introduced generated CO<sub>2</sub> into barium chloride and a sodium-hydroxide solution and made it absorb, by titrating with a hydrochloric-acid standard solution, it carried out the quantum of the CO<sub>2</sub> amount, and converted and calculated it from the CO<sub>2</sub> amount.

[0051] Next, the capacity maintenance factor after preservation was measured under hot environments about the produced cylindrical cell. The capacity maintenance factor after preservation is a ratio when saving a cylindrical cell for 50 days under an environment with a temperature of 45 degrees C, measuring the discharge capacity at the time of 5 cycle  
\*\*\*\*\*, and \*\* (ing) discharge capacity of 5 cycle eye by initial capacity under hot environments.

[0052] The result of the capacity maintenance factor under the amount of these residual lithium carbonates and hot environments is shown in Table 1.

[0053]

[Table 1]

	CO <sub>2</sub> 濃度 (体積%)	露点 (°C)	処理温度 (°C)	残存炭酸リチウム量 (重量%)	容量維持率 (%)
実施例 1	0.1	-15	23	0.42	92
実施例 2	5	-15	23	0.43	93
実施例 3	10	-15	23	0.42	95
実施例 4	50	-15	23	0.42	94
実施例 5	100	-15	23	0.44	92
実施例 6	10	-15	150	0.42	92
実施例 7	10	-15	23	0.42	91
比較例 1	0.03	-15	23	0.08	75
比較例 2	10	0	23	0.88	76
比較例 3	10	6	23	0.72	74
実験例 1	10	-15	200	0.78	74

[0054] From an X diffraction measurement result and the result of Table 1, it is thought by carrying out concentration of CO<sub>2</sub> in an ambient atmosphere to more than 0.1 volume % that the lithium hydroxide and lithium oxide which remain in positive active material were able to be lithium-carbonate-ized.

[0055] The amount of residual lithium carbonates has little CO<sub>2</sub> concentration of an ambient atmosphere at 0.03 volume %, and the capacity maintenance factor under hot environments is also smaller than the time of CO<sub>2</sub> concentration being 0.1 volume % so that the result of the example 1 of a comparison may show on the other hand. There are many the lithium hydroxides and lithium oxide with which CO<sub>2</sub> concentration remains in 0.03 volume %, without being lithium-carbonate-ized in positive active material, consequently it thinks that the capacity

maintenance factor under hot environments also falls, and this is \*\*\*\*.

[0056] Moreover, if the result of the example 2 of a comparison and the example 3 of a comparison is seen, there are many amounts of residual lithium carbonates, and the capacity maintenance factor is small. Since the dew-point is high, this is guessed because positive active material decomposed, a decomposition product and CO<sub>2</sub> reacted and the amount of lithium carbonates has increased with the moisture in an ambient atmosphere. Furthermore, since the positive active material itself has decomposed, it is surmised that the capacity maintenance factor became small.

[0057] Furthermore, in the example 1 of an experiment, although temperature of an ambient atmosphere was made into 200 degrees C, there are many amounts of residual lithium carbonates, and the capacity maintenance factor is small. In a temperature field higher than 150 degrees C, the decomposition reaction of positive active material occurs and this is conjectured that a decomposition product and CO<sub>2</sub> reacted and the amount of lithium carbonates has increased. Since the positive active material itself has furthermore decomposed, it is surmised that the capacity maintenance factor became small. Therefore, as for the temperature of an ambient atmosphere, it is desirable that it is 150 degrees C or less.

[0058] The lithium hydroxide and lithium oxide in positive active material can be lithium-carbonate-ized by carrying out CO<sub>2</sub> concentration in [ after calcinating a lithium multiple oxide ] an ambient atmosphere to more than 0.1 volume %, and making a dew-point into -15 degrees C or less from these results, and it turns out that the nonaqueous electrolyte rechargeable battery using this positive active material can obtain a high capacity maintenance factor under hot environments. Furthermore, gassing by CO<sub>2</sub> is understood that it is desirable to carry out below 150 degrees C.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view showing the configuration of the telescopic cell which applied this invention.

[Description of Notations]

1 Positive Electrode, 2 Negative Electrode, 3 Separator, 4 Electric Insulating Plate, 5 Cell Can, 6 Obturation Gasket, 7 Cell Lid, 8 Relief Valve Equipment, 9 PTC Component, 10 Positive-Electrode Charge Collector, 11 Negative-Electrode Charge Collector, 12 Positive-Electrode Lead, 13 Negative-Electrode Lead

---

[Translation done.]



\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

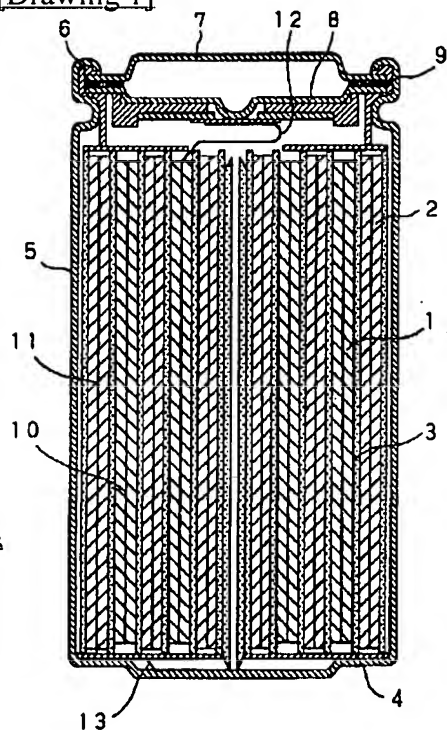
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DRAWINGS

---

[Drawing 1]



---

[Translation done.]